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In re Patent Application of Mario LECLERC et al.	
U.S. Patent Application No. 10/003,774	Docket No.: 146617.00000
Filed: October 31, 2001	
For: CONJUGATED POLYCARBAZOLE DERIVATIVES AND PROCESS FOR THE PREPARATION THEREOF	

E.H.G.  
2/1/02  
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**CLAIM FOR PRIORITY**

Sir:

The benefit of the filing date of the following priority application filed in the following foreign country is hereby requested, and the right of priority provided in 35 U.S.C. 119, is hereby claimed.

In support of this claim, filed herewith is a certified copy of said original foreign application:

Canadian Patent Application No. 2,324,757 filed October 31, 2000.

Respectfully submitted,

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Dated: February 7, 2002

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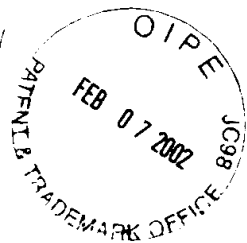


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Specification and Drawings, as originally filed, with Application for Patent Serial No:  
**2,324,757**, on October 31, 2000, by **UNIVERSITÉ LAVAL**, assignee of Mario Leclerc  
and Jean-François Morin, for "Conjugated Polycarbazole Derivates and Process for the  
Preparation Thereof".

*[Signature]*  
Agent certificateur/Certifying Officer

November 19, 2001

Date

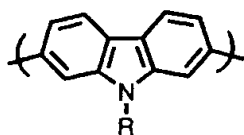
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## ABSTRACT

The invention relates to conjugated polycarbazole derivatives comprising repeating or alternating units of the formula:



wherein R is a linear or branched alkyl group containing 1 to 22 carbon atoms. The conjugated polycarbazole derivatives according to the invention have interesting optical and electrochemical properties which render them suitable for use in the manufacture of diverse electrical, optical and electro-optical devices

- 1 -

## CONJUGATED POLYCARBAZOLE DERIVATIVES AND PROCESS FOR THE PREPARATION THEREOF

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The present invention pertains to improvements in the field of conjugated polymers. More particularly, the invention relates to conjugated polycarbazole derivatives and to a process for the preparation thereof.

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A conjugated polymer is a polymer which possesses a delocalized pi-electron system along its backbone as described, for example, by D.J. Sandman in "Trends in Polymer Science", Vol. 2, p. 44 (1994).

15

Conjugated polymers are considered as a very important class of electroactive and photoactive materials by both academic and industrial laboratories. The synthesis over the last twenty years of highly pure polyacetylene, polythiophenes, polyphenylenes, polyfluorenes, ladder polymers, and other conjugated polymers optimized physical properties has led to a significant improvement in the performance of these polymeric materials and to a better understanding of their structure-property relationships. However, up to now, only poorly conjugated poly(N-alkyl-3,6-

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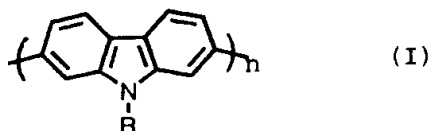
carbazole) derivatives are available so that these cannot be used for the development of light-emitting diodes, electrochromic windows, electrochemical sensors, photovoltaic cells, photoconductors, photorefractive materials, etc.

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It is therefore an object of the present invention to provide conjugated polycarbazole derivatives having improved optical and electrochemical properties.

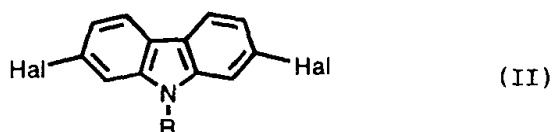
According to one aspect of the invention, there is provided a conjugated poly(N-alkyl-2,7-carbazole) of formula (I):

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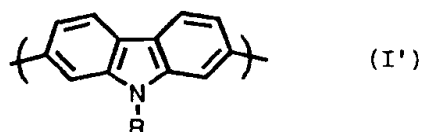
wherein R is a linear or branched alkyl group containing 1 to 22 carbon atoms, and n is an integer of about 3 to about 100.

- 5           The present invention also provides, in another aspect thereof, a process for preparing a conjugated poly(N0alkyl-2,7-carbazole) of the formula (I) defined above, which comprises treating a N-alkyl-2,7-dihalocarbazole of formula (II):



- 10       wherein R is as defined above and Hal is a halogen atom selected from the group consisting of bromine, chlorine and iodine atoms, with triphenylphosphine and 2,2'-bipyridine in the presence of zinc and nickel chloride to cause polymerization of the compound of formula (II).

- 15           According to a further aspect of the invention, there is provided a conjugated polymer comprising alternating units of formula (I'):



wherein R is as defined above.

- 20           The conjugated polycarbazole derivatives according to the invention, comprising repeating or alternating units of formula (I') have interesting optical and electrochemical properties which render them suitable for use in the manufacture of light-emitting diodes, electrochromic windows, electrochemical sensors, photovoltaic cells, photoconductors, photorefractive materials and the like.

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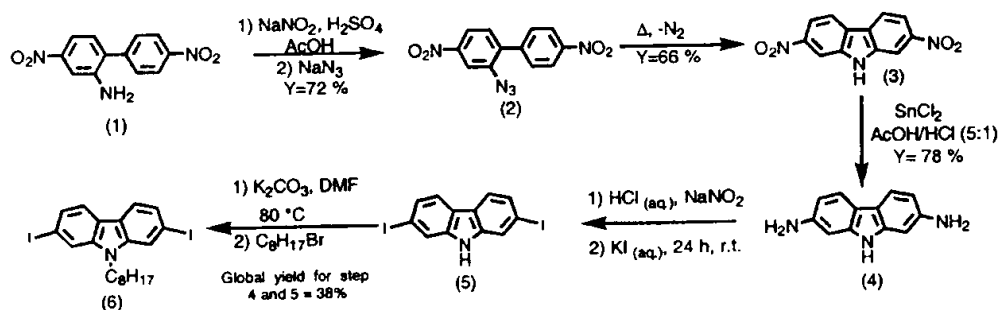
The following non-limiting examples illustrate the invention, reference being made to the accompanying drawings in which:

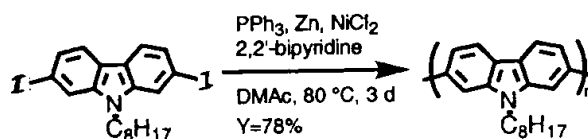
Figure 1 is the absorption (Abs.) and emission (PL) spectra of poly(N-octyl-2,7-carbazole) in chloroform and in the solid state; and

Figure 2 is the cyclic voltammogram of poly(N-octyl-2,7-carbazole) cast on a platinum electrode, in acetonitrile containing 0.1M *n*-Bu<sub>4</sub>NBF<sub>4</sub>, at a scan rate of 10 mV/s.

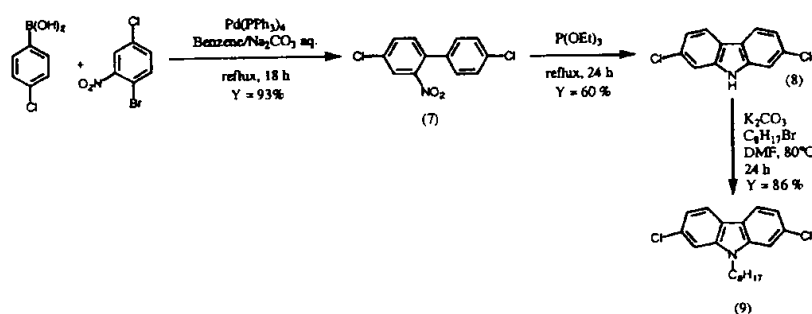
#### EXAMPLE 1: Preparation of poly(N-octyl-2,7-carbazole)

Following the procedure developed by Smith and Brown, 4,4'-dinitro-2-biphenylamine (Aldrich Co.) was treated with NaNO<sub>2</sub> and NaN<sub>3</sub> to give the  
 10 corresponding azide via the transformation of the amino group into a diazonium salt. A ring closure reaction, assured by a nitrene intermediate, was carried out to give 2,7-dinitrocarbazole in a 66 % yield. This compound was then reduced using SnCl<sub>2</sub> in a mixture of acetic acid/HCl (5 : 1) to give 2,7-diaminocarbazole in a 78 % yield. Then,  
 15 the amino groups of the resulting product were transformed to iodine atoms; the reaction was carried out in a 3M HCl solution using NaNO<sub>2</sub> and KI. N-octyl-2,7-diiodocarbazole was prepared in a 93% yield from 2,7-diiodocarbazole upon reaction with K<sub>2</sub>CO<sub>3</sub> and 1-bromooctane in anhydrous DMF at 80 °C. All monomers were characterized by NMR and mass spectrometry. Homopolymerization was achieved by a Yamamoto reaction described in Macromolecules, Vol. 25, p. 1214 (1992), using  
 20 N-octyl-2,7-diiodocarbazole as the starting material and triphenylphosphine, 2,2'-bipyridine, zinc and NiCl<sub>2</sub> as catalysts. Poly(N-octyl-2,7-carbazole) was obtained in a 78 % yield. The synthetic scheme is summarized as follows:





Alternatively, N-alkyl-2,7-dichlorocarbazole derivatives can be  
 5 obtained from a different synthetic pathway, according to the following scheme:



This scheme involves a coupling between 4-chlorophenylboronic acid (Aldrich Co.)  
 10 and 1-bromo-4-chloro-nitrobenzene (Aldrich Co.), followed by a ring closure using  
 P(OEt)<sub>3</sub> and an alkylation of the nitrogen atom in DMF and K<sub>2</sub>CO<sub>3</sub> using 2-  
 ethylhexylbromide.

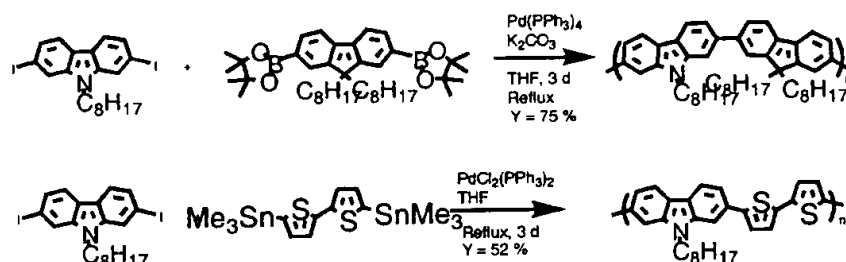
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**EXAMPLE 2** : Preparation of poly(N-octyl-2,7-carbazole-*alt*-9,9-dioctyl-2,7-  
 fluorene) and poly[N-(2-ethylhexyl)-2,7-carbazole-*alt*-5,5'-(2,2'-bithiophene)].

Alternating copolymers were prepared from Suzuki couplings  
 20 (described by Ranger, M. et al. in *Macromolecules*, Vol. 30, p. 768 (1997) between  
 di-boronic functionalized aromatic units and N-alkyl-2,7-diiodocarbazole derivatives.  
 Poly(N-octyl-2,7-carbazole-*alt*-9,9-dioctyl-2,7-fluorene) was prepared from a reaction

between 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene and N-octyl-2,7-diiodocarbazole using  $(\text{Ph}_3)_4\text{Pd}(0)$  as catalyst in a mixture of THF and 2 M  $\text{K}_2\text{CO}_3$  aqueous solution. Moreover, Stille couplings (described by Yu, L. et al. in Acc. Chem. Res., Vol. 29, p. 13 (1996)) between distannyl aromatic derivatives and N-alkyl-2,7-diiodocarbazole derivatives are possible. As an example, poly[N-(2-ethylhexyl)-2,7-carbazole-*alt*-5,5'-(2,2'-bithiophene)] was obtained with a good yield from N-(2-ethylhexyl)-2,7-diiodocarbazole and of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, in presence of  $\text{Cl}_2(\text{PPh}_3)_2\text{Pd}(0)$  in THF. These polymerization reactions are summarized in the following scheme:

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**Materials.** All chemicals were purchased from Aldrich Co. and were used without further purification. 4,4'-dinitro-2-azidobiphenyl (2) and 2,7-dinitrocarbazole (3) was obtained by using procedures to those reported by Smith *et al.*<sup>9,10</sup>

**4,4'-dinitro-2-azidobiphenyl (2):** To a solution of 10.0 g (0.039 mol) of 4,4'-dinitro-2-biphenylamine in a mixture of 200 mL of acetic acid and 40 mL of sulfuric acid at 0°C was added dropwise 5.32 g (0.078 mol) of sodium nitrite. The mixture was stirred at 5-10°C for 2h after 5g of urea (to destroy the excess nitrous acid), 500 mL of ice-water and 5 g of activated carbon was added. The cold suspension was stirred again for 20 min and filtrated rapidly through a büchner funnel into a flask immersed in an ice bath. A solution of 5.07 g (0.078 mol) of sodium azide in 100 mL of water was added dropwise to the yellow clear filtrate. The resulting solution was stirred at 0°C for 1 h and at room temperature for 24 h. The mixture was quenched with 500 mL of a solution of  $\text{NaHCO}_3$  in water and extracted three times with ethyl acetate. The



organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. Recrystallization in ethanol afforded 7.4 g of the title product as a yellow solid. M.P.: 171-172°C (Yield: 72%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 8.37 (d, 2H, *J* = 8.8 Hz); 8.20 (d, 1 H, *J* = 2.2 Hz);  
5 8.16 (dd, 1H, *J* = 10.3 and 2.2 Hz); 7.89 (dd, 2H, *J* = 8.8 and 2.8 Hz); 7.79 (d, 1H, *J* = 8.1 Hz).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): 143.84; 140.35; 137.98; 133.20; 131.81; 124.29; 120.71; 115.44.

HRMS: Calculated for C<sub>12</sub>H<sub>7</sub>N<sub>5</sub>O<sub>4</sub>: 285.0498 Found: 285.0505

10

**2,7-dinitrocarbazole (3):** To 600 mL of boiling kerosene (first washed with concentrated sulfuric acid) was added very slowly 6.0 g (0.021 mol) of compound 2. The solution was maintained to reflux for 1 h. After cooling, the solution was kept at 4°C for 24 h. The precipitate was filtered through a büchner funnel and the solid was  
15 washed with petroleum ether. Very pure material was obtained by recrystallization in ethanol to afforded 3.38 g of the title product. M.P.: >300°C. (Yield: 66 %).

<sup>1</sup>H NMR (300 MHz, Acetone-*d*<sub>6</sub>, ppm): 11.41 (s, 1H); 8.55 (d, 2H, *J* = 2.2 Hz); 8.49 (d, 2H, *J* = 8.8 Hz); 8.15 (dd, 2H, *J* = 8.8 and 2.2 Hz).

<sup>13</sup>C NMR (75 MHz, Acetone-*d*<sub>6</sub>, ppm): 141.07; 126.38; 122.09; 114.76.

20 HRMS: Calculated for C<sub>12</sub>H<sub>7</sub>N<sub>3</sub>O<sub>4</sub>: 257.0436 Found: 257.0431

**2,7-diaminocarbazole (4).** To a solution of 2,7-dinitrocarbazole (6.0g, 23.3 mmol) in a mixture of acetic acid (200 mL) and hydrochloric acid (35 mL) was added 44.3 g (0.23 mol) of tin(II) chloride. The mixture was refluxed for 24 h under argon. After  
25 cooling, the precipitate was separated from the solvent by filtration and washed several times with cold acetic acid. The resulting diammonium salt was dissolved in water followed by addition of an aqueous solution of sodium hydroxide until the pH was around 10. The precipitate was collect by filtration and dried under vacuum. Recrystallization in ethanol afforded 3.6 g of the title product as a shiny gray solid.  
30 M.P. 248°C (dec.). (Yield: 78 %).

<sup>1</sup>H NMR (300 MHz, Acetone-*d*<sub>6</sub>, ppm): 9.45(s, 1H); 7.53(d, 2H, *J* = 8.1 Hz) ; 6.62 (d, 2H, *J* = 1.5 Hz); 6.47 (dd, 2H, *J* = 17.0 and 2.2 Hz); 4.45 (s, 4H).

<sup>13</sup>C NMR (75 MHz, Acetone-*d*<sub>6</sub>, ppm) : 146.53; 142.53; 119.72; 116.58; 108.70; 96.42.

HRMS: Calculated for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>: 197.0953

Found: 197.0948

5 **2,7-diiodocarbazole (5).** To a solution of 1.5 g (7.6 mmol) of compound (4) in 100 mL of 3 M HCl solution at 0°C was added very slowly 1.1 g (16 mmol) of sodium nitrite in 5 mL of water. The mixture was stirred at 0°C for 2 h and then added to 100 mL of a solution of potassium iodide in distilled water. The stirring was kept for 24 h at room temperature. The precipitate was collect by filtration and washed with  
10 aqueous solution of NaHCO<sub>3</sub>. The solid was dried under vacuum for 24 h and use directly in the next reaction without further purification. However, the crude material could have been purified by column chromatography (silica gel, 10 % ethyl acetate in hexanes as eluent) but the reaction yield would be greatly affected, probably due to the degradation of the product on silica gel.

15 <sup>1</sup>H NMR (300 MHz, Acetone-*d*<sub>6</sub>, ppm): 10.54(s, 1H); 7.93 (m, 4H) ; 7.53 (dd, 2H, *J* = 7.4 and 1.5 Hz).

<sup>13</sup>C NMR (75 MHz, Acetone-*d*<sub>6</sub>, ppm) : 141.77; 128.88; 122.69; 120.79; 120.74; 90.89.

HRMS: Calculated for C<sub>12</sub>H<sub>7</sub>I<sub>2</sub>N: 418.8668

Found: 418.8675

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***N*-octyl-2,7-diiodocarbazole (6).** To a solution of compound 5 (3,0 g) in 30 mL of DMF was added 0.66 g (4.9 mmol) of K<sub>2</sub>CO<sub>3</sub>. The solution was stirred at 80°C for 2 h under argon after 0.93 g (4.9 mmol) of bromooctane was added. The mixture was stirred at 80°C for 24 h and then quenched with 30 mL of water. The aqueous layer  
25 was extracted three times with 50 mL of diethyl ether. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexanes as eluent) followed by recrystallization in methanol to give 1.55 g of the title product as a white solid. M.P.: 82-84°C. (Global yield for the last two steps: 38 %).

30 <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 7.78 (d, 2H, *J* = 8.1 Hz); 7.73 (s, 1H); 7.52 (dd, 2H, *J* = 8.8 and 1.5 Hz); 4.17 (t, 2H, *J* = 7.4 Hz); 1.82 (m, 2H); 1.30 (m, 10 H); 0.88 (t, 3H, *J* = 5.9 Hz).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) : 141.25; 128.20; 121.84; 121.81; 117.96; 90.80; 43.25; 31.81; 29.28; 29.17; 28.80; 27.15; 22.64; 14.11.

HRMS: Calculated for C<sub>20</sub>H<sub>23</sub>I<sub>2</sub>N: 530.9920

Found: 530.9906

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**1-chloro-4-(4'-chlorobenzene)-2-nitrobenzene (7):** In a 100 mL flask, 4-chlorophenylboronic acid (2.0 g, 12.8 mmol, Aldrich), 1-bromo-4-chloro-2-nitrobenzene (2.72 g, 11.5 mmol, Aldrich), 18 mL of benzene and 12 mL of aqueous K<sub>2</sub>CO<sub>3</sub> 2M were mixed. The resulting solution was degassed with a vigorous flow of argon. Tetrakis(triphenylphosphine)Pd(0) (0.5-1.0 mol %) was then added under argon and the mixture was refluxed for 2h. The mixture was filtered through a Büchner funnel and the filtrate was extracted three times with diethyl ether. The combine organic layer was washed with brine and dried over magnesium sulfate. The solvent was removed and the residue was purified by column chromatography (silica gel, hexanes as eluent) to provide 2.87 g of the title product as a yellow solid. M.P. 88-89 °C (Yield: 93%).

<sup>1</sup>H NMR (300 MHz, Acetone-*d*<sub>6</sub>, ppm): 8.06 (d, 1H, *J* = 2.2 Hz); 7.82 (dd, 1H, *J* = 5.9 and 2.2 Hz); 7.61 (d, 1H, *J* = 8.8 Hz); 7.52 (dd, 2H, *J* = 8.8 and 2.2 Hz); 7.40 (dd, 2H, *J* = 8.1 and 2.2 Hz).

<sup>13</sup>C NMR (75 MHz, Acetone-*d*<sub>6</sub>, ppm) : 136.08; 134.97; 134.67; 134.15; 133.43; 130.43 (2C); 129.61; 124.88 (2C).

**2,7-dichlorocarbazole (8):** A 25 mL flask was charged with 2.0 g of compound 2 and 10 mL of triethylphosphite. The resulting mixture was refluxed under argon for 5 h. The excess of triethylphosphite was distilled under vacuum (30°C, 0.25 mm Hg) and the crude product was purified by column chromatography (silica gel, 10 % ethyl acetate in hexanes) to provides 1.05 g of the title product as a white solid. M.P.: 188-189°C (Yield: 60 %).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): 8.02 (s, 2H); 7.91 (d, 2H, *J* = 8.1 Hz); 7.38 (d, 2H, *J* = 1.5 Hz); 7.22 (dd, 2H, *J* = 8.8 and 1.5 Hz).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): 140.18; 131.86; 121.43; 121.10; 120.62; 110.87.

**N-((2-ethylhexyl)-2,7-dichlorocarbazole) (9):** To a solution of 0.9 g compound 3 (3.8 mmol) in 20 mL of DMF was added 1.06 g (7.7 mmol) of  $K_2CO_3$ . The solution was stirred at 80°C for 2 h under argon after 1.47 g (7.6 mmol) of 2-ethylhexylbromide was added. The mixture was stirred at 80°C for 24 h and then  
5 quenched with 30 mL of water. The aqueous layer was extracted three times with 50 mL of diethyl ether. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexanes as eluent) to give 1.15 g of the title product as a colorless oil (Yield = 86 %).

10  **$^1H$  NMR** (300 MHz,  $CDCl_3$ , ppm): 7.90 (d, 2H,  $J = 8.1$  Hz); 7.32 (d, 2H,  $J = 1.5$  Hz); 7.19 (dd, 2H,  $J = 8.8$  and 2.2 Hz); 4.01 (m, 2H); 2.01 (m, 1H); 1.33 (m, 8H); 0.90 (m, 6H).

**$^{13}C$  NMR** (75 MHz,  $CDCl_3$ , ppm): 141.74; 131.71; 121.01; 120.89; 119.81; 109.29; 47.64; 39.16; 30.87; 28.64; 24.40; 23.06; 14.03; 10.92.

15 **Poly (N-octyl-2,7-carbazole):** In a 10 mL flask, 1.00 g (1.9 mmol) of compound 6, 0.296 g (1.1 mmol) of triphenylphosphine, 0.405 mg (6.2 mmol) of zinc powder 99.998% 100 mesh, 0.015 g (0.09 mmol) of 2,2'-bipyridine 0.012 g (0.09 mmol) of anhydrous nickel (II) chloride and 3 mL of anhydrous DMAc were stirred under argon for 3 days at 80°C. The whole mixture was then poured into a cold mixture of  
20 methanol/HCl (5:1 v/v). The precipitated material was recovered by filtration through a Büchner funnel and washed with dilute HCl. The solid material was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting solid was dilute again in chloroform and filtrated on 0.2  $\mu m$  filtering paper to remove all traces of nickel. The resulting solid was dried under reduced pressure for  
25 24 h. (Yield: 78 %).

**Poly (N-octyl-2,7-carbazole-*alt*-9,9-dioctyl-2,7-fluorene).** In a 10 mL flask, 0.225 g (0.42 mmol) of compound 6, 0.271 g (0.42 mmol) of 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene and 10 mg of  $(PPh_3)_4Pd(0)$  were  
30 dissolved in a degassed mixture of THF (2.5 mL) and aqueous 2 M  $K_2CO_3$ . The solution was refluxed under argon for 3 days. The whole mixture was then poured into cold methanol (100 mL). The precipitated material was recovered by filtration

through a Büchner funnel and washed with dilute HCl. The solid material was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF and  $\text{CHCl}_3$ . (Yield: 78 %).

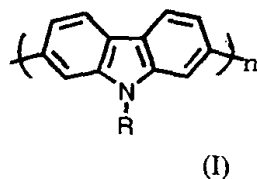
5 **Poly [N-2-ethylhexyl-2,7-carbazole-alt-5,5'-(2,2'-bithiophene)]**. In a 50 mL flask, 541 mg (1.1 mmol) of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, 531 mg (1.0 mmol) of N-2-ethylhexyl-2,7-diiodocarbazole and 25  $\mu\text{g}$  of  $\text{Cl}_2(\text{PPh}_3)_2\text{Pd}(0)$  were dissolved in 30 mL of degassed THF. The solution was refluxed under argon for 3 days. The whole mixture was then poured into cold methanol (300 mL). The  
10 precipitated material was recovered by filtration through a Büchner funnel and washed with dilute HCl. The solid material was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF and  $\text{CHCl}_3$ . (Yield: 52 %).

15 The resulting conjugated homopolymers and copolymers are soluble in common organic solvents, such as chloroform and tetrahydrofuran. The number-average molecular weight (measured by size exclusion chromatography against monodisperse polystyrene standards) of these polymers is about 10 kDa with a polydispersity of 2. They can be processed by spin coating or by simple casting to  
20 yield thin polymer films with good mechanical properties. As reported in Figure 1, the solution and solid-state optical properties of poly(N-octyl-2,7-carbazole) have been investigated in more details. In dilute solutions or as thin films, this polymer exhibits an absorption maximum around 380-390 nm, indicating a pale-yellow color in both forms. This absorption maximum is significantly red-shifted compared to that  
25 previously reported for poly(N-alkyl-3,6-carbazole)s (i.e. 300-320 nm) and can be related to a more conjugated structure. Moreover, poly(N-octyl-2,7-carbazole) exhibits an intense blue emission upon radiative excitation, with a quantum yield of about 80% in chloroform, at room temperature. In solution, poly(N-octyl-2,7-

carbazole) shows a maximum of emission at 417 nm followed by two vibronic side-bands at 439 and 474 nm whereas in the solid state, the polymer is slightly more conjugated with an emission maximum at 437 nm followed by two other maxima at 453 and 492 nm. These solid-state and solution emission spectra are slightly red-  
5 shifted compared to poly(9,9-dioctyl-2,7-fluorene) and could be related to the electron-donating effect of the nitrogen atom in the inner ring. Moreover, poly(N-octyl-2,7-carbazole) shows a relatively low oxidation potential at 0.75 V vs Ag/AgCl (Figure 2). This oxidation potential is lower than those reported for poly(N-alkyl-3,6-carbazole)s at 0.85 and 1.2 V vs Ag/AgCl and is an indirect proof of the more  
10 delocalized structure in 2,7-linked polycarbazoles. This combination of electrical and optical properties is particularly interesting for the development of a novel class of blue-light emitting materials. Moreover, with the possibilities of structural modifications through the synthesis of various alternating copolymers, it is possible to develop tunable light-emitting materials.

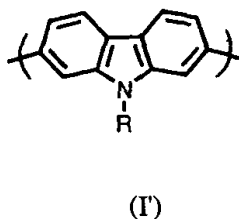
The embodiments of the invention, in which an exclusive property or privilege is claimed are defined as follows:

1. A conjugated poly(N-alkyl-2,7-carbazole) of formula (I):



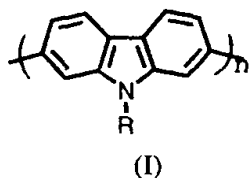
wherein R is a linear or branched alkyl group containing 1 to 22 carbon atoms and n is an integer of about 3 to about 100.

2. Poly(N-octyl-2,7-carbazole).
3. A conjugated polymer comprising alternating units of formula (I'):

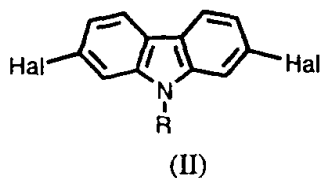


wherein R is a linear or branched alkyl group containing 1 to 22 carbon atoms.

4. Poly(N-octyl-2,7-carbazole-alt-9,9-dioctyl-2,7-fluorene).
5. Poly[N-2-ethylhexyl-2,7-carbazole-alt-5,5'-bithiophene)].
6. A process for preparing a conjugated poly (N-alkyl-2,7-carbazole) of formula (I):



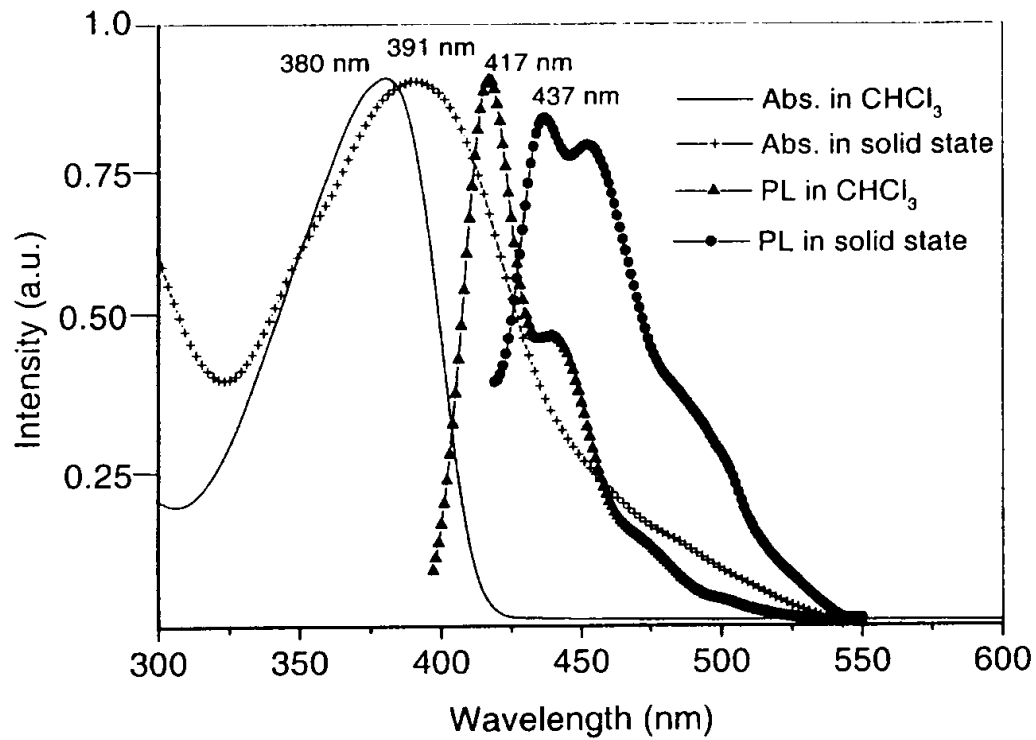
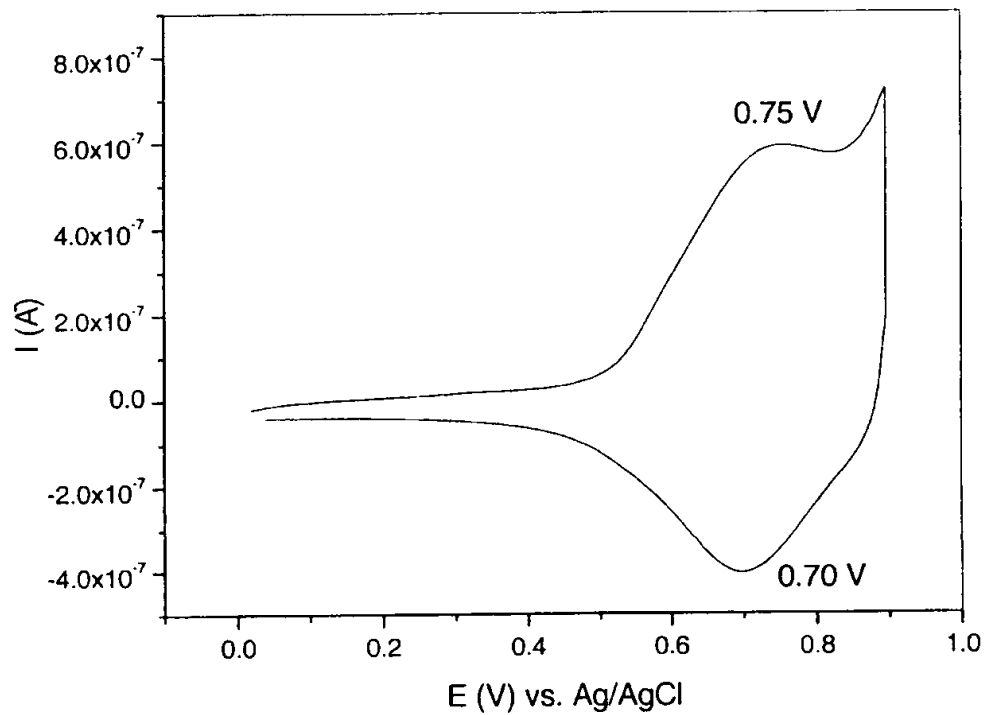
wherein R is a linear or branched alkyl group containing 1 to 22 carbon atoms and n is an integer of about 3 to about 100, which comprises treating a N-alkyl-2,7-dihaloindole of formula (II):



wherein R is as defined above and Hal is a halogen atom selected from the group consisting of bromine, chlorine and iodine atoms, with triphenylphosphine and 2,2'-bipyridine in the presence of zinc and nickel chloride to cause polymerization of the compound of formula (II).

7. A process according to claim 6, wherein use is made of a compound of formula (II) in which R is an octyl group and Hal is an iodine atom.



Fig. 1Fig. 2